Replacement of P-D-680 Solvents

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Background

Army and other Department of Defense (DoD) facilities have been and continue to experience problems using P-D-680, Dry cleaning and Degreasing solvent¹, for their maintenance activities. Currently, numerous federal, state, and local regulations impact usage of P-D-680 as a hazardous waste, a flammable material, a toxic substance, and an air pollutant². To resolve this problem, each of the services has initiated efforts to minimize P-D-680 solvent usage and to replace P-D-680 solvents with environmentally acceptable materials that are less hazardous and have effective cleaning performance. Under the auspices of the Joint Services Working Group (JSWG) on Minimization of Petroleum Distillate Solvents for Military Applications, the Fuels and Lubricants Technology Team of the Tank-Automotive and Armaments Research, Development, and Engineering Center (TARDOC) as the specification preparing activity for P-D-680 has been working to develop environmentally compliant alternatives to P-D-680 that would be able to meet military requirements. This program, resourced under the Defense Supply Center Richmond's (DSCR's) HAZMIN Program, was divided into the following two Phases.

Phase I: Conduct user surveys for P-D-680 solvents and evaluate commercial alternative solvents

Phase II: Conduct field validation tests, and revise the P-D-680 specification

- (a) Army and Air Force Applications
- (b) Navy Aviation and Shipboard Applications

All tasks of these Phases have been completed, and the test results and findings were summarized in this paper.

P-D-680 User Survey

The objectives of P-D-680 user survey were to determine what is viewed to be requirements for P-D-680 solvents, the positive and negative aspects of current solvents, and the characteristics of an "ideal" solvent replacement. Total fifty-four (54) responses were received from various installations operated by Army, Navy, Air Force, Marine Corps, National Guard, and NATO. Most users reported that P-D-680 solvents are excellent degreasers, have good corrosion protection properties, and are currently used for degreasing machine parts in equipment maintenance including helicopters. Twenty-five (25) percent use Type I, sixty-three (63) percent use Type II, and twelve (12) percent use Type III. The survey also indicated that Types I and II

solvents do not meet the numerous federal, state and local environmental regulations due to their high VOCs and low flash points. In conjunction with replacement of P-D-680 solvents, most users did not want to substitute other types except for petroleum based solvents in their applications due to the rusting, freezing and compatibility problems. Concerning the quality control of P-D-680 solvents, most users expressed negative responses in having a Quality Product List (QPL) for P-D-680 solvents because off-the-shelf products are more readily available. However, they want to have some quality control on P-D-680 solvents for safety. In this survey, P-D-680 users also expressed their own opinions on the requirements and constraints for an ideal P-D-680 solvent that can be used in their applications. These are summarized as follow:

- Effective clean and fast drying
- Low VOCs
- Low toxicity and low odor
- Low flammability (high flash point)
- Recyclable or biodegradable
- Material compatible
- Cost effective
- Corrosion protection

Laboratory Evaluation

Currently, numerous different types of cleaners/solvents are formulated for use in various of applications and are available in domestic markets. For the study, eighty-two (82) samples were evaluated and compared to P-D-680 solvents. These samples were originally solicited for evaluation as potential substitutes of P-D-680 solvents. Most solvents are currently used for general maintenance parts cleaning and were formulated with various chemical materials classified as aqueous, semi-aqueous, terpene and petroleum. To assess their physical and chemical properties, all samples were tested according to an established testing protocol. To provide baseline comparison data, P-D-680 solvents were also evaluated. The laboratory test results of candidate solvents were reported at the TARDEC technical report³ entitled "Replacement of P-D-680 Solvents for General Maintenance of DoD Equipment". Based on the laboratory tests, it revealed that only petroleum distilled hydrocarbon solvents and terpene/hydrocarbon solvents meet current P-D-680 performance requirements that reflect military needs. Especially, terpene/hydrocarbon blended solvents showed excellent performance in all requirements. These products are listed under the proposed Type IV. Unlike these solvents, aqueous types of solvents and water-based solvents do not lend themselves as candidate P-D-680 solvents due to their poor corrosion protection and solvency.

Initially, twenty-three (23) commercial solvents were found for candidate alternative P-D-680 solvents. Then, the typical eight (8) candidate solvents were selected for the next Phase study. These products provide excellent solvency, are currently listed as less hazardous solvents, and meet the federal and local environmental laws (i.e., RCRA). Table 1 lists the physical/chemical properties of typical eight (8) candidate solvents that were found in the laboratory evaluation.

Field Demonstration

In concert with the Phase II portion of this initiatives, the field demonstrations were conducted at DoD installations to verify performance and environmental applicability of candidate solvents under a variety of field environments. Table 2 summarizes field testing sites and solvents that were evaluated at each installation as well as identifying the cleaning procedure used and equipment. The major evaluation criteria used in this demonstration were odor, cleaning power, residue, corrosion protection and toxicity.

Fort Lewis evaluated seven (7) candidate solvents (Breakthrough, Unocal 150, Actrel 1171L, 134 Hi-solv, Skysol 100, PF, and Electron 296) in tactical vehicle maintenance shops and compared with P-D-680. The test results showed although the new solvents provided somewhat weaker solvency than P-D-680, they demonstrated good cleaning ability in a wide variety of soils, especially heavily contaminated grease, hydraulic fluid, engine oils, tar, carbon deposits and waxes. Most users reported the solvency of the terpene/hydrocarbon blended solvents was the same as the other types of candidate hydrocarbon solvents. All solvents tested in ground equipment provided adequate solvent power. No corrosion, residue and compatibility problems were reported. Two hydrocarbon solvents (Unocal 150, Actrel 1171L) were rejected due to their strong offensive odor, which may affect worker's health. However, citron odor was not a problem in the ground vehicle cleaning applications.

In aviation applications, Fort Lewis helicopter maintenance shop also evaluated Skysol 100 solvent using helicopter parts such as engines, rotors, and generators. etc. This shop is currently seeking a new environmentally complaint solvent in order to replace P-D-680 Type I which defined as a hazardous material due to its low flash point. The test results showed that the solvency of Skytel 100 solvent was adequate to clean soils contaminated in various types of aviation parts. No corrosion and compatibility problems were reported. Citron odor was not a major problem. However, some complaints related to slow drying time were received. Generally, Type II solvents provide slower drying time than Type I due to their higher flash points. This deficiency is minor and can be resolved using air dryers or ovens. Currently, Type II solvent is strongly recommended to replace the Type I as a means to reduce flammability problems.

P-D-680 solvents are also widely used in weapon cleaning applications. To verify the performance of candidate solvents in weapon applications, Fort Lewis evaluated three solvents (Breakthrough, Skysol, Skysol 100) using small arms such as the M16 rifle. The test results showed the performance of all candidate solvents was acceptable except for their odor characteristics. In these demonstrations, a strong citron odor was a major problem in closed areas of weapon cleaning facilities. Generally, the large variations of odor depend on human sensitivity and are very difficult to control in small closed area. Odorless products such as Breakthrough solvent were well accepted in both open and closed weapon cleaning facilities.

Ft. Hood also evaluated two (2) candidate solvents (Skysol 100, Breakthrough) in helicopter maintenance applications and weapon cleaning applications. Both solvents were very well accepted in all maintenance applications. Especially, most users indicated candidate solvents significantly

reduce the toxicity (i.e., skin irritation) when compared to P-D-680. Drying time of candidate solvents was the same as for P-D-680 Type II.

San Antonio Logistic Center at Kelly AFB evaluated three (3) candidate solvents (Breakthrough, Actrel 117L, and Electron 296). In aviation fuel injection repair shop, Breakthrough solvent was very well accepted in comparison to the Actrel 1171L solvent due to its odorless characteristics. Electron 296 solvent was also well accepted by aviation ground supporting equipment such as electric generators, No d-limon odor problem were reported.

Naval Surface Warfare Center (NSWC), Carderock Division, MD evaluated Breakthrough solvent using cartridge-type deep groove bearings coated with DOD-G-24508, Grease, High Performance, Multipurpose. For comparison purpose, a P-D-680 Type II solvent was also reevaluated using the same bearing cleaning procedure. The test results showed that Breakthrough solvent is superior to P-D-680 Type II in cleaning shipboard bearings lubricated DOD-G-24508 grease. It was noted that P-D-680 solvent had a longer drying time, left a residue, and did not breakdown the grease as quickly as the candidate solvent.

The Shore Intermediate Maintenance Agent (SIMA) of Naval Station, Mayport, FL also evaluated Breakthrough solvent using shipboard engine and missile components. This shop currently uses P-D-680 Type I as a regular cleaning agent. Based on the SIMA field demonstration, it was reported that the Breakthrough is acceptable solvent for the replacement of P-D-680 Type I in their shipboard applications because of its odorless characteristics and good cleaning performance.

Naval Air Warfare Center (NAWC), Patuxent River, MD also evaluated Breakthrough solvent in various aircraft supporting equipment such as compressor valve, bearings, intake oil breathers, etc. In a similar result, the Breakthrough solvent was accepted to clean soils from various types of aviation parts. No corrosion and compatibility problems were reported.

Naval Aviation Depot (NADEP), Cherry point, NC evaluated four (4) candidate solvents (Breakthrough, Electron 296, PF, 134 Hi-Solv) in various aviation and ground equipment (i.e., cargo aircraft, utility vehicles). All candidate solvents were well accepted as the replacement of P-D-680 solvents.

Solvent recycling is common practice in many industries and wide range of solvents are currently recycled using distillation techniques or filtration. Although a solvent recycling demonstration was not conducted in this study, most users observed that the recirculation parts washer actually served as a recycling unit and significantly extended solvent useful life.

Toxicity Clearance for Candidate Solvents

All candidate products are non-carcinogenic and do not contain any ingredients listed by EPCRA, CERCLA, and RCRA. Also, worker exposure is not regulated by OSHA. However, there is a new requirement for all new products entering the military supply system in that each is to be reviewed and given Toxicity Clearance by the Center for Health Promotion and Preventative Medicine (CHPPM). As a part of this program, CHPPM approved the toxicity clearance for six (6)

candidate solvents that were accepted.

Conclusions

On the basis of the work completed to date, the following Table lists environmentally compliant solvents that were found as acceptable replacements for P-D-680 solvents. Based on the DoD field demonstration, P-D-680 specification is being revised to accept new environmentally complaint solvents.

| Туре | Solvent composition | Candidate P-D-680 solvent |
|-----------------|---------------------------|-----------------------------------------|
| Ι | Hydrocarbon | Type II solvent |
| П | Hydrocarbon | Breakthrough |
| Ш | Hydrocarbon | 134 Hi-Solv Current Type III solvent |
| IV [*] | Terpene/Hydrocarbon Blend | Electron 295, PF Skysol, Skysol 100 |

^{*} This is a proposed new Type for P-D-680 and its performance is equivalent to Type II.

Also, the following findings evolved during this study.

- Severe hydrotreated odorless hydrocarbon solvents were very well accepted because their low odor characteristics and less toxicity.
- Hydrotreated terpene/hydrocarbon blended solvents were also very well accepted in all DoD applications. Citron odor was not considered as a major problem in open working area.
- Odor, cleaning power, corrosion protection and toxicity of solvent were major evaluation factors for all cleaning applications.
- P-D-680 Type II solvent had a long drying time, strong offensive odor, left residue, and did not break-down the grease as quickly as the candidate solvent. For these reason, most participants rejected the use of P-D-680 Type I and II solvents in their cleaning applicants.
- Low odor hydrotreated Type II hydrocarbon solvent was acceptable for weapon cleaning applications due to its odorless characteristics.
- All candidate solvents performed well for all applications when compared to P-D-680 solvent.
- Candidate Type II solvents were found to be acceptable when used in applications requiring Type I.

References

1. Federal Specification P-D-680, Dry Cleaning and Degreasing Solvent, 29 October, 1992.

- 2. Connie Van Brocklin, "Replacement of P-D-680 for Army Ground Vehicle and Equipment Applications", Letter report 94-1, October, 1993.
- 3. In-Sik Rhee, Carlos Venez, Karen Von Bernewitz, "Replacement of P-D-680 Solvents for General Maintenance of DoD Equipment", TARDEC Technical Report No. 13643, September, 1995.
- 4. In-Sik Rhee, Carlos Venez, "Field Demonstration for P-D-680 Solvent Replacement", TARDEC Technical Report No. TR-13730, October, 1996.
- 5. In-Sik Rhee, "Field Demonstration for P-D-680 Solvent Replacement (Part II)", TARDEC Technical Report No. TR-13751, May, 1998.

Table 1. Laboratory Solvent Test Results

| Product Code | Flash Point °C | Distilla | tion, °C | Kauri- Butanol value | Non- volatile residue, % | Aniline Point, °C | Odor | VOC g/l | Evap, %, @20 min | Corrosion | | Relative Solvency, % |
|------------------|----------------------|----------|----------|----------------------------|-----------------------------------|----------------------|----------|------------|---------------------|-----------|---------|----------------------------|
| | | I.B.P | D.P | | | | | | | Cu | Fe | |
| P-D-680 (1) | 47.0 | 165.4 | 204.6 | 39 | 0.1 | 61.2 | strong | 789.7 | 47.1 | 1a | no rust | 94.7 |
| P-D-680 (II) | 63.0 | 182.8 | 206.7 | 32 | 0.07 | 73.1 | strong | 785.8 | 22.8 | 1a | no rust | 94.4 |
| P-D680 (III) | 93.3 | 223.4 | 269.0 | 31 | 0.3 | 76.1 | odorless | 823.2 | 4.6 | 1a | no rust | 89.3 |
| Breakthroug h | 65.5 | 184.0 | 211.7 | 27 | 0.05 | 84.0 | odorless | 770 | 25.9 | 1b | no rust | 87.6 |
| Actrel 1171L | 81.1 | 211.6 | 241.1 | 30 | 0.35 | 77.8 | strong | 797 | 10.1 | 1a | no rust | 84.5 |
| Unocal 150 | 66.7 | 186.0 | 212.7 | 31 | 0.15 | 71.2 | mild | 772 | 19.1 | 1b | no rust | 90.2 |
| 134Hi-Solv | 97.8 | 232.4 | 299.3 | 24 | 0.07 | 94.5 | odorless | 796 | 3.8 | 1b | no rust | 80.7 |
| Skysol | 66.7 | 189.4 | 212.4 | 29 | 0.16 | 83.0 | citrus | 770 | 20.0 | 1b | no rust | 89.1 |
| Skysol 100 | 63.3 | 189.6 | 212.7 | 29 | 0.44 | 82.8 | citrus | 780 | 25.3 | 1a | no rust | 88.6 |
| Electron 296 | 63.9 | 191.8 | 235.6 | 32 | 0.01 | 69.1 | citrus | 782 | 18.1 | 1b | no rust | 87.8 |
| PF | 62.2 | 187.0 | 228.8 | 26 | 0.32 | 76.7 | citrus | 760 | 14.8 | 1b | no rust | 92.3 |

Table 2. Field Testing Sites for P-D-680 Replacement Solvents

| Military Installation | Candidate Solvent | Testing | Military Equipment | Cleaning Method | Specified | POC |
|-----------------------|-------------------------------|---------|-----------------------------|-------------------------------------------------|-----------------|----------------------|
| | | Site | | | Solvent | |
| Ft. Lewis | Breakthrough, Actrel1171L, | 18 | Ground Equipment, | Hand cleaning procedure | P-D-680 Types I | Ms. Cynthia K. Trout |
| | Unocal 150, 134 Hi- | | Helicopter, Weapon system | using IT-30 parts washers | and II | Tel: 206-967-3268 |
| | Solv, Skysol, Skysol 100, | | | | | |
| | Electron 296, PF | | | | | |
| Ft. Hood | Breakthrough, Skysol 100 | 4 | Helicopter, Weapon system, | Hand cleaning procedure | P-D-680 Type II | Mr. R.J. Holley |
| | | | Small arms | using IT-48 parts washers | | Tel: 817-287-7145 |
| Kelly Air Force Base | Breakthrough, Actrel 1171L, | 2 | Aircraft, ground supporting | Ultrasonic and Hand | P-D-680 Type II | Mr. Marlin Baggett |
| · | Electron 296 | | equipment | cleaning procedure using existing parts washers | 71 | Tel: 210-925-7391 |
| NADEP, Cherry | Electron 296, 134 Hi-Solv, | 5 | Aviation, ground supporting | Spray buster and Hand | P-D-680 Types I | Ms. Jacki Grant |
| Point | Breakthrough, PF | 3 | equipment | cleaning procedure using | and II | Tel: 919-464-7164 |
| Tomit | Dicakunough, 11 | | equipment | parts washers | and II | 101. 919-404-7104 |
| NSWC, Carderock | Breakthrough, P-D-680 Type II | 1 | Shipboard groove bearings | Hand cleaning procedure | P-D-680 Type II | Ms. Mary L. Wenzel |
| Division | | | | using a parts washer | | Tel: 301-227-5359 |

| Naval Station, | Breakthrough | 1 | Shipboard engine and | Hand cleaning procedure | P-D-680 Type I | Mr. Bob Tierney |
|----------------|--------------|---|----------------------|----------------------------|-----------------|-------------------|
| Mayport | | | missile components | using a IT-48 parts washer | | Tel: 904-270-6730 |
| NAWC, Patuxent | Breakthrough | 1 | Aircraft supporting | Hand cleaning procedure | P-D-680 Type II | Mr. Don McLaurin |
| River | | | equipment | using a IT-30 parts washer | | Tel: 301-342-7989 |